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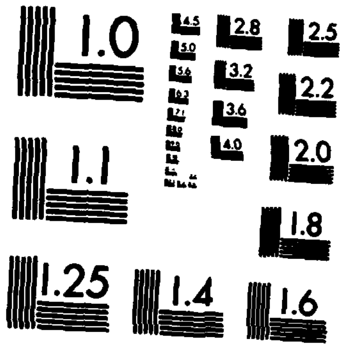

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Structure-to-Property Relationships in Addition Cured Polymers II - Resin T_g and Composite Initial Mechanical Properties of Norbornenyl Cured Polyimide Resins

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NASA

STRUCTURE-TO-PROPERTY RELATIONSHIPS IN ADDITION CURED POLYMERS II — RESIN Tg AND COMPOSITE INITIAL MECHANICAL PROPERTIES OF NORBORNENYL CURED POLYIMIDE RESINS

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Abstract

PMR (polymerization of monomeric reactants) methodology was used to prepare thirty different polyimide oligomeric resins. Monomeric composition as well as chain length between sites of crosslinks were varied to examine their effects on glass transition temperature (Tg) of the cured/postcured resins. An almost linear correlation of Tg versus molecular distance between the crosslinks was observed. An attempt was made to correlate Tg with initial mechanical properties (flexural strength and interlaminar shear strength) of unidirectional graphite fiber composites prepared with these resins. However the scatter in mechanical strength data prevented obtaining as clear a correlation as was observed for the structural modification/crosslink distance versus Tg. Instead, only a range of composite mechanical properties was obtained at the test temperatures studied (room temperature, 288 and 316 °C). Perhaps more importantly, what did become apparent during the attempted correlation study was (a) that PMR methodology could be used to prepare composites from resins that contain a wide variety of monomer modifications, and (b) that these composites almost invariably provided satisfactory initial mechanical properties as long as the resins selected were melt processable.

1. INTRODUCTION

As a continuation of an initial phase[1] of a larger investigation directed towards understanding the high temperature degradation of addition cured polymers, a wide variety of norbornenyl cured resins were fabricated as both neat resin discs and unidirectional graphite fiber composites.

The variable in this portion of the study was structural modification of the monomers between the norbornenyl endcaps. The purpose of this study was twofold. The first was to determine if any relationships existed on glass transition temperature (Tg) versus changing the distance and/or monomer variation between the norbornenyl crosslink sites. The second purpose was to determine if any relationships could be correlated between any structural modification/Tg relationship observed and the composite initial mechanical strengths obtained.

2. EXPERIMENTAL

Three dianhydrides (pyromellitic dianhydride (PMDA), 2,2-bis (3,4-dicarboxyphenyl)-hexafluoropropane dianhydride (HFDA), and 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA)) and three mixtures of these dianhydrides were reacted as their respective diacid-dimethyl esters with up to ten different aromatic diamines and a norbornenyl endcap (Nadic Ester, NE). These reactions provided a wide variety of monomeric polyimide precursor mixtures at a stoichiometry of N/N+1/2. All the reactions were accomplished using PMR (polymerization of monomeric reactants) methodology.[2,3] The compositions investigated were selected on the basis of providing (a) a systematic variation in monomer compositions, and (b) melt processable resins suitable for composite fabrication. All three dianhydrides and mixtures of these were used with 4,4'-methylenedianiline (MDA) and 4,4'-diaminotriphenylmethane (DATPM) as the aromatic diamines. Other monomer combinations selected were all singular HFDA or BTDA based resins containing a variety of aromatic diamines at stoichiometries such that a constant formulated molecular weight (FMW) of 1500 was maintained. In a few cases where the stoichiometries varied widely in order to maintain FMW = 1500, additional resin compositions were selected to maintain similar stoichiometries while letting FMW vary widely. All these compositions, their stoichiometries and FMW's (when not equal to 1500) are indicated in the left half of Table 1. These selected compositions and the MDA and DATPM compositions were fabricated into neat resin discs and unidirectional unsized Celion 6000 graphite fiber composites. A total of thirty different composites and corresponding neat resin discs were prepared for this study. The resin discs were used to characterize the glass transition temperatures (Tg) via thermomechanical analysis (TMA) before and after 16 hr postcures in air at 316 °C. The TMA heat-up rate was 20 °C/min while the postcure heat-up rate was 100 °C/hr. The composites were cured/postcured using a standard PMR-15 316 °C cure/postcure methodology[2,3] in order to maintain as similar a processing cycle as

possible for the resin discs and composites.

The flexural strength and interlaminar shear strength (ILSS) of the thirty postcured composites were determined, usually in triplicate, at room temperature and 316 °C according to ASTM test methods described in Ref. 4. Mechanical tests were also performed at 288 °C for resins which exhibited Tg's too close to the 316 °C test temperature. Fiber content was maintained as close to 65 wt % fiber (approximately 60 vol % fiber) as possible. However when the resulting laminate deviated from this composition the flexural data was normalized to this composition.

3. RESULTS AND DISCUSSION

3.1 Structure to Tg Relationships

The Tg's of all the MDA and DATPM based resins are shown in Figs. 1 to 3. Several consistent trends in the Tg's before and after postcure versus varying the molecular chain length (but not molecular structures) between the norbornenyl crosslinks are observed in these figures. First, the Tg before postcure was always less than the cure temperature and the Tg always increased during 316 °C postcure. In the compositions with shorter distances between crosslinks (lower N values) the Tg after 316 °C postcure exceeded the cure temperature. The magnitude of the Tg increases during the 316 °C postcure, as shown by the distance between the two lines in each figure, was similar regardless of the variation in the distance between the norbornenyl crosslinks (N value). Second, the Tg's either before or after 316 °C postcure always increased with decreasing distance between the norbornenyl crosslinks (lower N). This Tg increase was a linear function of the distance between the crosslinks.

Several trends in the Tg's before and after postcure versus varying the molecular structures (but not monomer stoichiometry, N) between the norbornenyl crosslinks are observed in Fig. 4. These trends were seen by systematically replacing BTDA (in the BTDA/MDA composition) with PMDA while maintaining a constant stoichiometry at N = 2.087. This could also be considered as an effect of decreasing the distance between norbornenyl crosslinks (as seen earlier in Figs. 1 to 3) because of the linear, shorter structure of PMDA compared to BTDA. First, as before, the Tg before postcure was always less than the cure temperature and the Tg always increased during 316 °C postcure. In the compositions with the greater amounts of PMDA the Tg after 316 °C postcure also exceeded the cure temperature. The magnitude of the Tg increase during 316 °C postcure, as shown by the distance between the two lines in Fig. 4, was also similar regardless

of the variation in the extent of BTDA replacement by PMDA. Second, the Tg's either before or after 316 °C postcure also always increased with increasing amounts of PMDA. This increase was also a linear function of the amount of PMDA used to replace BTDA.

3.2 Structure/Tg to Composite Initial Mechanical Property Relationships

The ILSS of all the BTDA or HFDA/MDA or DATPM/NE composites were examined as a function of decreasing Tg (increasing N) and significant trends were not observed. The flexural strength data lead to a similar observation. At room temperature the composite mechanical properties appeared to be quite insensitive to the Tg and only sensitive to fiber content. At elevated test temperatures (288 and 316 °C) the composite mechanical properties appeared to show only a very slight decrease with decreasing Tg (or increasing distance between crosslinks) as long as the Tg > test temperature. However, the mechanical property data was scattered and a linear correlation was not observed.

The ILSS and flexural strength of the BTDA/PMDA//MDA/NE composites were also examined as a function of decreasing Tg (decreasing PMDA content, see Figs. 5 and 6). As before, at room temperature the composite mechanical properties were quite insensitive to the Tg (or changing BTDA/PMDA composition). However, at 316 °C the composite mechanical properties showed an increase with increasing PMDA content. Again, as before the scatter in the mechanical property data was such that a clear linear correlation was not observed. In addition, it should be noted that laminates prepared at 100 percent PMDA composition tended to crack in the unidirectional fiber direction and the corresponding resin discs also cracked during curing. Thus, although increasing PMDA content is a method of achieving higher Tg's, a decrease in resin processability/laminate quality was observed when PMDA content exceeded 75 percent. This is probably the cause of the nonlinear 100 percent PMDA ILSS data point in Fig. 6.

The remainder of the composites prepared for this study (all without MDA or DATPM) are identified in Table 1. In the right half of Table 1 were identified the maximum resin process temperatures and the resultant unpostcured and 316 °C postcured Tg's of these resin compositions. Visual inspections of the as processed composite structural integrity and comparisons of the Tg's indicated that all these resins (in Table 1) did provide satisfactory fabricated resin discs and composites. However because of the nature of the singular data points for each composition, trends were not readily

apparent that related the structural modifications effects on Tg to composite initial mechanical properties. Figures 7 and 8 demonstrate this by showing flexural strength and ILSS of all these composites only as a range of strengths at three test temperatures. The composites are grouped into two categories, those with and without MDA or DATPM as the diamine used in the polyimide. The majority of the resin compositions in Table 1 (without MDA or DATPM) provided a relatively small range of resulting strengths. When strengths were lower, the result could usually be attributed to either a low Tg or a resin deficient laminate. However almost all the MDA or DATPM compositions always provided an even narrower range of resulting strengths as shown by the MDA or DATPM strength range beside the non-MDA or non-DATPM range in figures 7 and 8. This suggests that the use of MDA or DATPM in norbornenyl resins may lead to a more consistent range of composite initial mechanical properties.

4. CONCLUDING REMARKS

In conclusion, the application of PMR technology to the preparation of composites containing a variety of structural modifications was successful as long as the resin composition selected was a melt processable monomer combination. Whether or not based on MDA or DATPM, these composites invariably exhibited satisfactory initial room temperature mechanical properties. As long as the Tg is sufficiently above the test temperature, these composites all invariably also exhibited satisfactory elevated temperature initial mechanical properties. The only exception to this conclusion was some monomer combinations, such as the 100 percent PMDA composition, instead led to increased brittleness and thus did not provide satisfactorily fabricated laminates.

5. REFERENCES

1. W.B. Alston, "Structure-to-Property Relationships in Addition Cured Polymers I. - Thermo-oxidative Stability of Norbornenyl Cured Polyimide Resins," Polymer Preprints, Volume 28, Number 2, 193rd ACS National Meeting, Anaheim, CA, Sept. 7-12, 1986.
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6. BIOGRAPHY

Dr. William B. Alston is presently a Materials Research Engineer with the Propulsion Directorate of the U.S. Army Aviation System Command, assigned to the Polymers Branch of the NASA-Lewis Research Center since 1971. He received his B.S. in Chemistry from the University of Wisconsin, M.S. and Ph.D. in Chemistry from the University of Iowa. His current research is in the high temperature polymer composite areas of monomer and polymer synthesis, crosslinking methods and matrix resin characterization.

TABLE 1

Identification of all Compositions Studied as Composites, Other Than Those Containing MDA or DATPM, and Their Formulations, Resin Processing Temperatures, and Tg's

Diamines used in HFDA compositions	N[a]	Resin final process temperature, °C	Tg	
			No postcure	Postcure[b]
3,3'-diaminobenzophenone	1.60	335	213	260
4,4'-diaminobenzophenone	1.60	330	209	277
2,7-diaminofluorene	1.67	342	281	325
4,4'-oxydianiline	1.66	325	286	316
paraphenylenediamine	[a]1.67 (1263)	325	315	350
paraphenylenediamine	2.13	316	300	355
4,4'-ethylenedianiline	1.60	336	250	380
4,4'-ethylenedianiline	[a]2.087 (1800)	316	248	370
1,1-bis(4-aminophenyl)-1-phenyl-2,2,2-trifluoroethane	1.15	334	292	345
Diamines used in BTDA compositions				
3,3'-diaminobenzophenone	2.00	340	208	269
4,4'-thiodianiline	[a]2.087 (1550)	330	257	239
4,4'-ethylenedianiline	2.00	390	300	360
3,3'-diaminodiphenylsulfone	1.79	333	239	273
4,4'-oxydianiline	2.083	316	270	321
1,1-bis(4-aminophenyl)-1-phenyl-2,2,2-trifluoroethane	1.377	316	275	351
	[a]2.087 (1950)	316	266	335
	[a]2.808 (2400)	316	258	322

[a]All resins at FMW = 1500 except those marked with a different (FMW).
[b]All resins postcured for 16 hours in air at 316 °C.

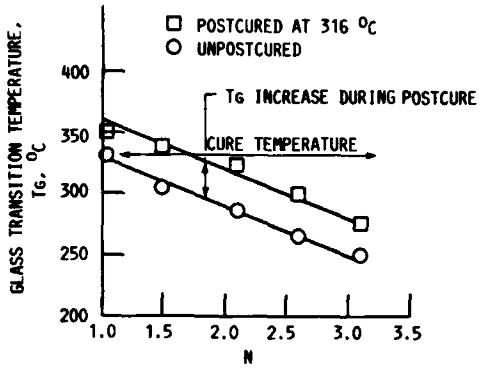
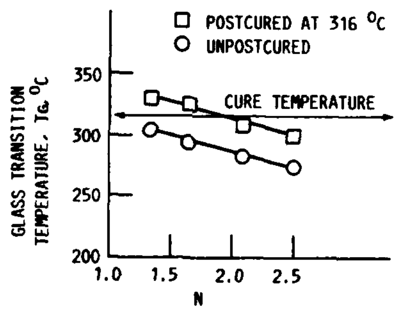


FIGURE 1.- EFFECT OF CHAIN DISTANCE BETWEEN CROSSLINKS ON TG OF BTDA/MDA/NE COMPOSITIONS.



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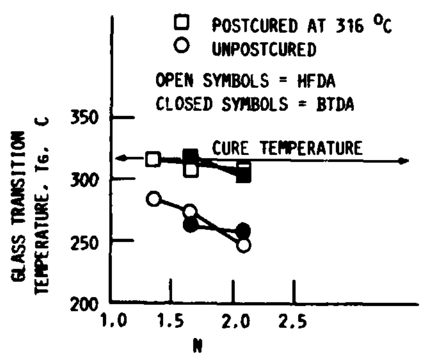

FIGURE 3.- EFFECT OF CHAIN DISTANCE BETWEEN CROSSLINKS ON TG OF BTDA OR HFDA/DATPM/NE COMPOSITIONS.

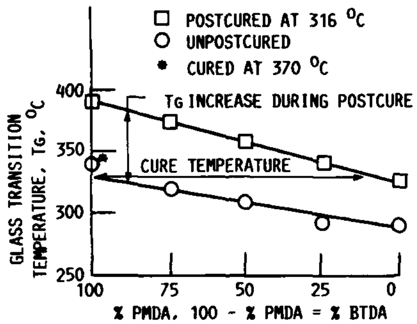

FIGURE 4.- EFFECT OF PMDA CONTENT ON TG OF MIXED PMDA/BTDA//MDA/NE COMPOSITIONS, ALL AT N = 2.087.

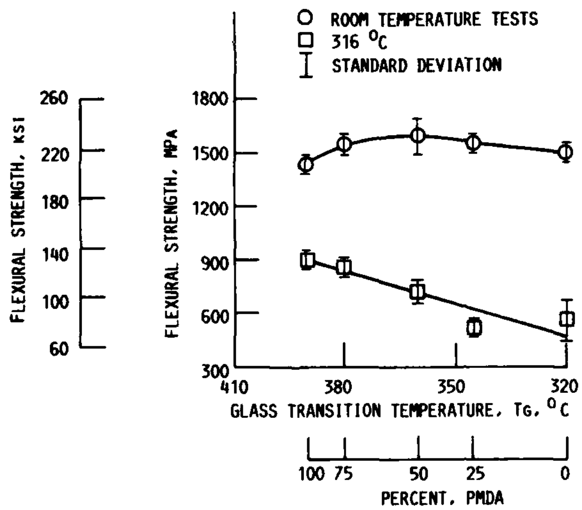

FIGURE 5.- EFFECT OF DECREASING TG (DECREASING PMDA CONTENT) ON FLEXURAL STRENGTH OF BTDA/PMDA//MDA/NE COMPOSITES.

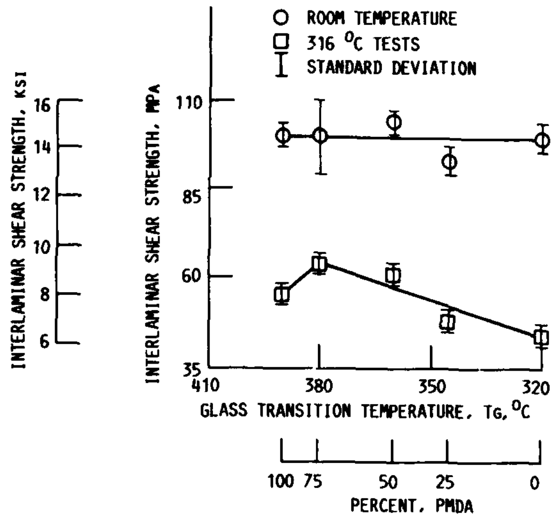

FIGURE 6.- EFFECT OF DECREASING TG (DECREASING PMDA CONTENT) ON INTERLAMINAR SHEAR STRENGTH, ILSS, OF BTDA/PMDA//MDA/NE COMPOSITES.

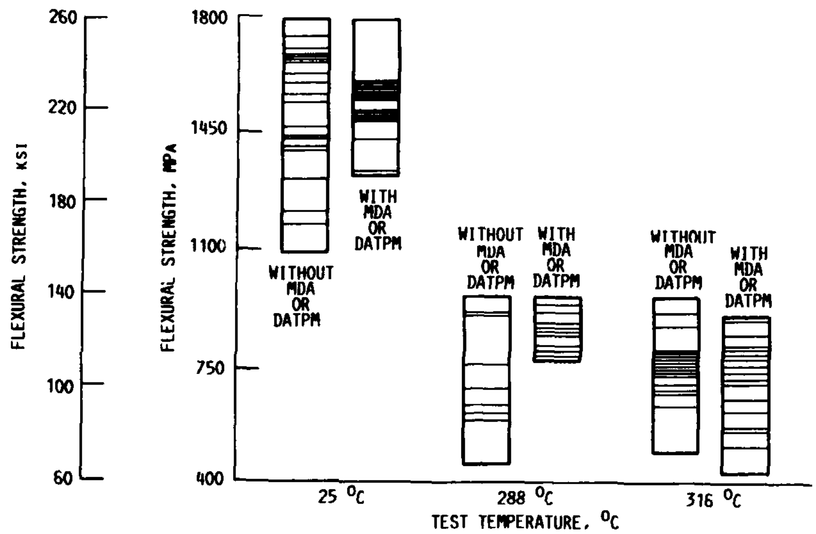

FIGURE 7.- RANGE OF AVERAGE COMPOSITE FLEXURAL STRENGTHS, NORMALIZED TO 60 VOL % FIBER (~65 WT % FIBER) FOR ALL MONOMER COMBINATIONS, DIVIDED INTO TWO CATEGORIES OF WITH AND WITHOUT MDA OR DATPM.

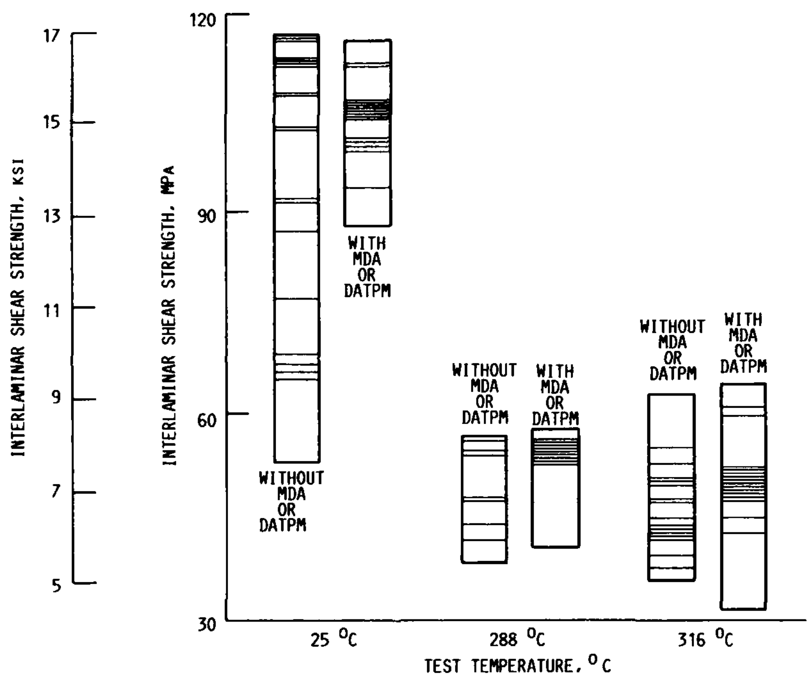

FIGURE 8.- RANGE OF COMPOSITE AVERAGE INTERLAMINAR SHEAR STRENGTH FOR ALL MONOMER COMBINATIONS, DIVIDED INTO TWO CATEGORIES OF WITH AND WITHOUT MDA OR DATPM.

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15. Supplementary Notes

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16. Abstract

PMR (polymerization of monomeric reactants) methodology was used to prepare thirty different polyimide oligomeric resins. Monomeric composition as well as chain length between sites of crosslinks were varied to examine their effects on glass transition temperature (Tg) of the cured/postcured resins. An almost linear correlation of Tg versus molecular distance between the crosslinks was observed. An attempt was made to correlate Tg with initial mechanical properties (flexural strength and interlaminar shear strength) of unidirectional graphite fiber composites prepared with these resins. However the scatter in mechanical strength data prevented obtaining as clear a correlation as was observed for the structural modification/crosslink distance versus Tg. Instead, only a range of composite mechanical properties was obtained at the test temperatures studied (room temperature, 288 and 316 °C). Perhaps more importantly, what did become apparent during the attempted correlation study was (a) that PMR methodology could be used to prepare composites from resins that contain a wide variety of monomer modifications, and (b) that these composites almost invariably provided satisfactory initial mechanical properties as long as the resins selected were melt processable.

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